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Emerging energy-efficiency and CO_2 emission-reduction technologies for cement and concrete production: A technical review

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ABSTRACT

Globally, the cement industry accounts for approximately 5 percent of current anthropogenic carbon dioxide (CO_2) emissions. World cement demand and production are increasing significantly, leading to an increase in this industry's absolute energy use and CO_2 emissions. Development of new energy-efficiency and CO_2 emission-reduction technologies and their deployment in the market will be key for the cement industry's mid- and long-term climate change mitigation strategies. This paper is an initial effort to compile available information on process description, energy savings, environmental and other benefits, costs, commercialization status, and references for emerging technologies to reduce the cement industry's energy use and CO_2 emissions. Although studies from around the world identify a variety of sector-specific and cross-cutting energy-efficiency technologies for the cement industry that have already been commercialized, information is scarce and/or scattered regarding emerging or advanced energy-efficiency and low-carbon technologies that are not yet commercialized. This paper consolidates available information on eighteen emerging technologies for the cement industry, with the goal of providing engineers, researchers, investors, cement companies, policy makers, and other interested parties with easy access to a well-structured database of information on these technologies.

Contents

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1. Introduction

The cement industry accounts for approximately 5 percent of current anthropogenic carbon dioxide (CO_2) emissions worldwide [1]. World cement demand and production are increasing; annual world cement production is expected to grow from approximately 2540 million tonnes (Mt) in 2006 to between 3680 Mt (low estimate) and 4380 Mt (high estimate) in 2050. The largest share of this growth will take place in China, India, and other developing countries on the Asian continent (Fig. 1) [2]. This significant increase in cement production is associated with a significant increase in the cement industry's absolute energy use and CO_2 emissions.

The production of 1 metric ton (t) of cement releases an estimated 0.73–0.99 t CO_2/t cement depending on the clinker-per-cement ratio and other factors. A major difference between the cement industry and most other industries is that fuel consumption is not the dominant driver of CO_2 emissions. More than 50 percent of the CO_2 released during cement manufacture, or approximately 540 kg CO_2 per t of clinker [3], is from calcination in which limestone ($CaCO_3$) is transformed into lime (CaO) in the following reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

The rest of the CO_2 emitted during cement manufacture is the result of burning fuel to provide the thermal energy necessary for calcination to occur. Kilns in which calcination takes place are heated to around 1400–1500 °C. Typically, energy accounts for 30–50 percent of cement production costs. Also, an average 100–110 kWh of electricity is consumed per t of cement [4]. The share of CO_2 emissions from electricity use is, on average, 5 percent of the total CO_2 emissions in the cement industry. Depending on the energy source and the efficiency at which it is used in the local electricity mix, this figure can vary from less than 1 percent to more than 10 percent [4]. As noted above, some 5 percent of CO_2 emissions are associated with quarry mining and transportation [4].

Studies have documented the potential to save energy and reduce CO_2 emissions by implementing commercially-available energy-efficiency technologies and measures in the cement industry worldwide [5–8]. Worrell et al. found total technical potential primary energy savings equal to 45% of 1994 energy use for cement making in the U.S [5]. Hasanbeigi et al. found the total technical potential for electricity and fuel saving in a group of 16 NSP kiln plants in China equal to 40% and 8% of total electricity and fuel used in the studied cement plants in 2008, respectively [6]. However, today, given the projected continuing increase in absolute cement production, future reductions (e.g., by 2030 or 2050) in absolute energy use and CO_2 emissions will require further innovation in this industry. Innovations will likely include development of different processes and materials for cement production or technologies that can economically capture and store the industry's CO_2 emissions. The development of these emerging technologies and their deployment in the market will be a key factor in the cement industry's mid- and long-term climate change mitigation strategies.

Many studies from around the world have identified sector-specific (e.g., [9–11]) and cross-cutting (e.g., [12]) energy-efficiency technologies for the cement industry that have already been commercialized. However, information is scarce and scattered regarding emerging or advanced energy-efficiency and low-carbon technologies for the cement industry that have not yet been commercialized. This paper consolidates available information on emerging technologies for the cement industry with the goal of

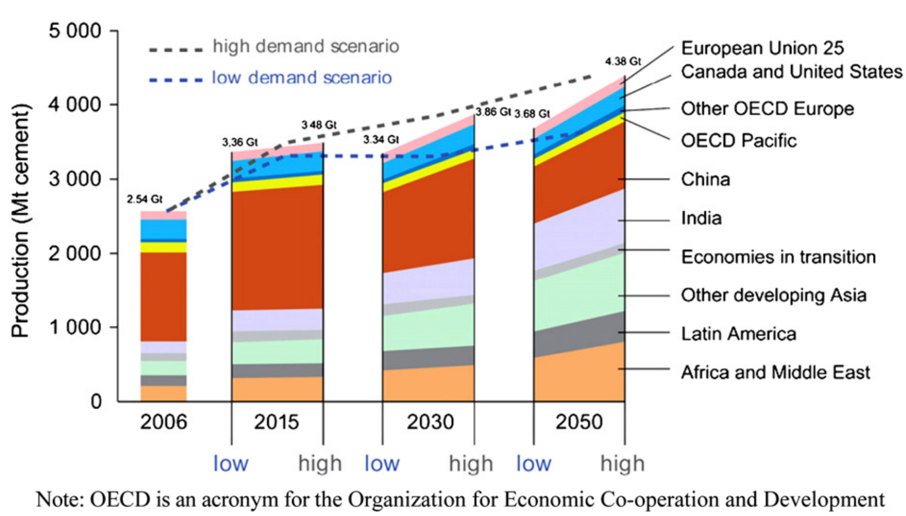


Fig. 1. Annual world cement production (WBCSD/IEA 2009b). *Note*: OECD is an acronym for the Organization for Economic Co-operation and Development.

giving engineers, researchers, investors, cement companies, policy makers, and other interested parties easy access to a well-structured database of information on this topic.

This paper also includes the concrete production sector because cement is the essential binding agent in concrete. Concrete is used worldwide as a building material and is the second-most-consumed substance on earth after water. Global concrete production is approximately 5.3 billion cubic meters per year [13]. Many emerging technologies focus on alternative materials and processes to reduce the carbon footprint of concrete. The information presented in this paper is collected from publically available sources [1–72]. Although the paper covers the main emerging energy-efficiency and low-carbon technologies for cement and concrete production, the list of emerging technologies addressed is not exhaustive.

The information about the 18 technologies covered in this paper is presented using a standard structure for each technology. First, we briefly describe the technology, including background, theory, pros and cons, barriers and challenges, and case studies if available. Next, we present the energy, environmental, and other benefits of the technology as well as cost information if available. For most technologies, we include a block diagram or picture. Finally, we identify the commercialization status of each technology along with resources for further information. The commercialization status for each technology is as of the writing of this paper and uses the following categories:

- Research stage: the technology has been studied, but no prototype has been developed
- Development stage: the technology is being studied in the laboratory, and a prototype has been developed
- Pilot stage: the technology is being tested at an industrial-scale pilot plant
- Demonstration stage: the technology is being demonstrated and tested at the industrial scale in more than one plant but has not yet been commercially proven
- Semi-commercial stage: the technology is proven and is being commercialized but has a very small market share.

The nature of emerging technologies is that many are proprietary and/or the primary source of information about them is the manufacturers who are developing them. In some cases, we mention the names of companies that are developing or providing a technology so that readers can obtain more information about the company and the product. It should be noted that the purpose of this paper is solely informational. Finally, because the nature of emerging technologies is a constant and rapid change, the information presented in this paper is also subject to change. If readers are aware of a new technology that is not presented in this paper or have updated information about a technology that is described in this report, please contact the authors of the report.

2. Emerging energy-efficiency and CO_2 emission-reduction technologies

The subsections below describe emerging technologies to reduce energy consumption and CO_2 emissions in the different steps of the cement production process, as well as emerging alternative raw materials and products for cement and concrete production. Table 1 shows the list of the 18 emerging technologies presented in this paper and makes a comparison for some of their characteristics.

2.1. Emerging grinding technologies

High-activation grinding is the main emerging grinding technology described below; other emerging technologies are mentioned briefly.

2.1.1. High-activation grinding

One strategy for conserving materials and reducing energy use in cement production is to increase the amount of elements other than Portland cement in blended cement products. However, increased use of other elements can result in a final product that is slow to develop compressive strength. One solution that has

Table 1
Emerging technologies for cement and concrete production and a comparison of their benefits and commercialization status.

No.	Category/Technology name	(Potential) Benefits		Commercial status				
		Energy saving	CO_2 reduction	Research	Development	Pilot	Demo	Semi-commercial
	Emerging grinding technologies							
1	High activation grinding	X	X					X
	Emerging kiln technologies							
2	Fluidized bed kiln	X	X				X	
	Emerging alternative raw material technologies							
3	Calcareous oil shale as an alternative raw material	X	X			X		
4	Use of steel slag as kiln raw material - CemStar® Technology	X	X					X
5	Non-carbonated raw material for cement production		X					X
6	Cement with low lime saturation factor	X	X					X
	Emerging alternative cement products							
7	Cement and construction materials based on magnesium oxide	X	X			X		
8	Geopolymer cement	X	X				X	
9	Cement primarily of fly ash and recycled materials	X	X					X
	Emerging carbon capture technologies for the cement industry							
10	Capturing the CO_2 resulting from limestone precalcination		X	X				
11	CO_2 sequestration in concrete curing technology	X	X		X			
12	Carbonate looping technology		X		X			
13	Bio-technological carbon capture		X		X			
14	Oxy-fuel technology	X	X			X		
15	Post-combustion carbon capture using absorption technologies		X			X		
16	Calera process		X			X		
17	Industrial recycling of CO_2 from cement process into high-energy algal biomass		X				X	
18	**Use of nanotechnology in cement and concrete production**	X	X	X				

Table 2
Emerging grinding technology for the cement industry.

Technology name	Energy/Environment/Other benefits	Commercial status	References
High activation grinding	● No waste material; the grinding process does not pollute air or water. ● Process is enclosed, with required dust protection features. ● For every t of clinker replaced by additives from mechanical activation grinding, the avoided energy uses are approximately: ○ Thermal energy: 3.0 to 6.5 GJ/t clinker ○ Electricity: 60 to 100 kWh/t clinker (European Commission 2010)[a] ● The electricity used for mechanical activation ranges from 30–50 kWh/t product [29], and should be deducted from aforementioned savings. ● Other avoided emissions (from clinker production and kiln fuel use) include sulfur dioxide (SO_2) and nitrogen oxides (NO_x).	Semi-commercial	[29,39–41,56,57]

[a] The electricity used for mechanical activation grinding should be deducted from these savings.

been researched to improve compressive strength development is using high-energy milling to mechanically increase the reactivity of some of the blended constituents, i.e., fly ash and slag [41]. Mechanical activation or enhanced reactivity of fly ash or blast furnace slag in cement results from the combined effects of increased surface area and physiochemical changes produced by vibratory or attrition milling [40].

Kumar et al. [39–41] studied mechanically-induced reactivity of blast furnace slag and fly ash. They found that up to 65 percent of the clinker in blended cement could be replaced with milled fly ash. The strength of the resulting product was comparable to that of commercial cement containing only 20–25 percent fly ash. The increased reactivity and reduced water requirements of attrition and vibratory milled fly ash are attributed to the fact that, with these milling techniques, the small (<1 μm) cenospheres of the fly ash retain their original shape. In contrast, grinding fly ash in a ball mill destroys most of the cenospheres. Because the cenospheres remain intact in mechanically-activated fly ash, the resulting hydrated cement demonstrates lower porosity and improved strength compared to a product made with ball-milled fly ash. Kumar et al. [39] also studied the use of mechanically-activated granulated blast furnace slag (GBFS) used in place of 50–95 percent of the clinker in Portland slag cement. Test results showed that Portland slag cement containing 80–85 percent mechanically-activated GBFS was much stronger than typical commercial Portland slag cement, which contains 35 percent slag. Both 1-day and 28-day strength were found to increase [39]. Table 2 shows the energy, environmental and other benefits as well as commercialization status of this technology.

The EMC Cement Company produces energetically modified cement (EMC) and pozzolana using a commercialized technology based on mechanical activation concepts. EMC's plant began operating near Jewett, Texas, in September, 2004, with an initial production capacity of about 150,000 t/year, which can be increased to meet demand. Waste fly ash from a power plant is conveyed directly to the EMC production facility [29].

Other emerging grinding technologies: Ultrasonic comminution efficiently transfers to the raw material the energy needed for crushing, by means of acoustic ultrasonic pulses that are generated by two counter-rotating disks with special aerodynamic surfaces. The small-pulse durations exert pressure waves that pulverize the particles. Ultrasonic comminution was introduced in 2003 and has only been tested at a model scale for slag grinding. There are currently proposals for additional research, and scaling up to industrial dimensions is under consideration. Plasma comminution is another emerging grinding technology. It is performed in a liquid and uses shock waves. It has been tested on semiconductor materials [56,57].

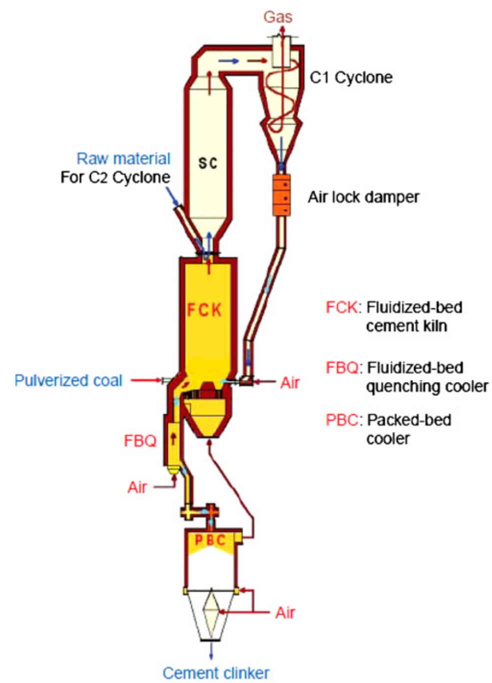


Fig. 2. Schematic of fluidized-bed cement firing kiln system [44].

2.2. Emerging kiln technologies

2.2.1. Fluidized bed kiln

A fluidized bed kiln (FBK) burns raw materials into powder with granules 1.5–2.5 mm in diameter. FBK uses a new technology known as granulation control/hot self-granulation [44], which agglutinates part of the raw material powder to form a core and attaches other raw material powder around the core. A FBK replaces the traditional rotary kiln with a stationary vertical cylindrical vessel (reactor) where the raw materials are calcined in a fluidized bed (Fig. 2). An overflow at the top of the reactor regulates the transfer of clinker to the cooling zone. FBKs have improved heat recovery rates compared to conventional rotary kilns (burn to 1,400 °C and cool to 100 °C in a two-stage cooler) [30]. The advantages of a FBK are anticipated to be lower capital costs, lower operating temperatures, fewer NO_x emissions, lower overall energy use, and ability to accept a wide variety of fuels. However, it is difficult to scale up the current FBK demonstrations to the required 5000–6000 t/day (tpd) clinker capacity [72]. Early FBK technologies were not commercially successful because of high clinker recycling rates. Today, FBK development is in

progress in Japan and the U.S. A FBK with a clinker capacity of more than 1000 tpd was being erected in China in 2009 but it is not clear whether or not it is in operation now [11].

Based on a feasibility study of a plant with a clinker capacity of 3000 tpd as well as the actual operation history (from 1986 to1995 by Sumitomo Osaka Cement Co. Ltd, Japan) of a 200-tpd clinker capacity plant, FBKs could achieve the following compared to a conventional rotary kiln: (1) reduction of heat use and CO_2 levels by 10–12 percent, (2) a NO_x emission level of 380 mg/Normal cubic meter (Nm^3) or less, (3) maintenance of current SO_x emissions levels, and (4) reduction of construction cost and installation area by 30 percent [30]. Table 3 shows the energy, environmental and other benefits as well as commercialization status of this technology.

2.3. Emerging technologies for alternative raw materials

Table 4 shows the energy, environmental and other benefits as well as commercialization status of the emerging technologies for the use of alternative raw materials. The description of each technology is presented below.

2.3.1. Calcareous oil shale as an alternative raw material

Calcareous oil shale can be used as an alternative feedstock and partial fuel substitute in clinker production. If oil shale is burned separately, the resulting ash can be used as an additive in finish grinding. Partially decarbonated oil shale can also be used to reduce CO_2 emissions from the calcination process. Oil shale may have caloric value that will contribute to the energy requirements in the precalciner and/or the kiln. To be used as a feedstock, oil shale must be ground to $< 90\ \mu m$ [35]. Oil shale can reportedly be used for 8–10 percent of the raw meal in the kiln. Oil shale has already been used in some cement plants in Germany and Russia [32,70].

2.3.2. Use of steel slag as raw material for the kiln—CemStar® technology

For steel manufacturing, calcium oxide or lime (CaO) is added to molten steel at 1650 °C to remove impurities such as silica, magnesium, aluminum, and other oxides. These impurities float to the top and are poured away as slag [48]. The CemStar® process was first developed in 1994 by Texas Industries (Midlothian, Texas). This process uses electric arc furnace slag as input to the cement kiln in place of limestone [9]. During the kiln pyroprocess, $^3/_4$-in.- to 1-in.-diameter slag is added to the feed end of the kiln as a component of the raw material mix. Because of its lower melting point (1260 °C–1316 °C), the slag does not require additional fuel in the kiln to form clinker with other raw feed components. Moreover, mineralizers already present in the slag help catalyze clinker formation. In addition, the exothermic reaction of converting dicalcium silicate into tricalcium silicate, which happens when slag is exposed to the high temperature, releases supplementary heat into kiln, resulting in even higher efficiency of the cement manufacturing process [48].

The CemStar® process eliminates the need to grind the slag because it allows the addition of 2 cm slag lumps directly to the kiln (using large lumps has traditionally led to poor clinker formation). Depending on the location of the slag injection, the CemStar® process might also save heating energy (calcination energy is estimated to be 1.9 GJ/t clinker). Because there is already calcined lime in the slag, the CemStar® process results in reduced CO_2 emissions from calcination. The lower combustion energy conditions and flame temperatures also lead to a decrease in NO_x emissions [9]. Traditional clinker production expansion methods are typically very costly and time consuming, requiring significant resources and disrupting continuous facility operations. CemStar® offers significant production and operational advantages including improved production rates of clinker, minimal capital investment requirements, no additional fuel consumption, and stable kiln operations. CemStar® technologies can be installed with minimal disruption in continuous kiln operation [48]. For example, Texas Industries has licensed its patented CemStar cement production process to Rio Grande Portland Cement Company in Mexico [65].

2.3.3. Non-carbonated raw material for cement production—use of carbide slag

Carbide slag, also known as calcium carbide residue (CCR), is an unavoidable solid-waste byproduct of the industrial production of ethyne, polyvinyl chloride, polythene alcohol, and other products. A large amount of carbide slag from industrial production causes serious pollution in the surrounding environment, especially in water. Because there are no other appropriate disposal methods, carbide slag is currently disposed of in landfills [67]. In conventional cement production, limestone is decarbonated in the pyroprocessing stage (main reaction: $CaCO_3 \rightarrow CaO + CO_2$) to produce CaO (the main content of clinker) and CO_2; this accounts for more than half of the CO_2 emissions during clinker production. To decrease the CO_2 emissions, CCR can be used to partially replace limestone as a raw material. Calcium hydroxide [$Ca(OH)_2$], the main content of CCR, produces CaO and water (H_2O) during pyroprocessing (e.g., in a cement kiln) without CO_2 emissions (main reaction: $Ca(OH)_2 \rightarrow CaO + H_2O$). Thus, using CCR will substantially reduce CO_2 emissions from cement production [67].

Using CCR in cement kilns entails the following steps [66]:

1) CCR dehydration and transportation
2) Grinding and storage

Table 3
Emerging kiln technology for the cement industry.

Technology Name	Energy/Environment/Other benefits/Costs	Commercial status	References
Fluidized bed kiln	• FBK energy use is expected to be 10 to 15 percent lower than that of conventional rotary kilns. • NO_x emissions are reduced to 0.77 kg/tonne clinker, compared to 2.1 to 2.6 kg/tonne clinker for conventional kilns, because of lower combustion temperatures in the FBK [72]. • Future FBK fuel consumption is estimated at 2.66 to 3.1 GJ/t clinker. This might be less than that of conventional rotary kilns but not of modern precalciner rotary kilns, which have demonstrated fuel use of 2.7 to 2.8 GJ/t clinker [72]. CSI/ECRA (2009) reports that the FBK reduces thermal energy use by up to 300 megajoules (MJ)/t clinker but increases the electricity used by approximately 9 kWh/t clinker [11]. • FBKs might produce clinker with lower alkali content than is found in clinker from conventional rotary kilns. • An FBK needs less space and has greater flexibility with respect to raw material feed than conventional rotary kilns [72].	Demonstration stage	[11], [44], [72]

Table 4
Emerging alternative raw material technologies for cement production.

Technology name	Energy/Environment/Other benefits/ Costs	Commercial status	References
Calcareous oil shale as an alternative raw material	• Energy use could be reduced by 74 MJ/t cement if oil shale is used to make up 8 percent of the raw meal in cement production. • Assuming that oil shale replaces 8 percent of the raw meal, an investment of $1/t cement would be required to install a feed system. Operating costs would increase by $0.08/t cement assuming the shale source is close to the cement manufacturing facility. • The reduction in CO_2 emissions from using oil shale is directly related to the amount of limestone feedstock replaced by the shale and the caloric value of the shale [70].	Pilot stage	[32], [35], [70]
Use of steel slag as kiln raw material—CemStar® Technology	• CemStar® technology increases clinker production by up to 15 percent compared to the conventional process. • CemStar® technology allows replacement of 10 to 15 percent of clinker by electric arc furnace slag. • Using 10 percent slag would reduce energy consumption by 0.19 GJ/t, CO_2 emissions by roughly 11 percent, and NO_x emissions by 9 to 60 percent, depending on kiln type and plant specific conditions [9], [48]. • Equipment costs are mainly for handling materials and vary from $200,000 to $500,000 per installation. Total investments are approximately double the equipment costs. CemStar® charges a royalty fee. • Cost savings result from increased income from additional clinker produced without increased operation and energy costs. • Cost savings also come from reduced iron ore purchases because the slag helps to meet iron needs in the clinker. • In 1999, the U.S. Environmental Protection Agency (U.S. EPA) awarded special recognition to the CemStar® process in the U.S. as part of the ClimateWise program [9].	Semi-commercial	[9], [48]
Non-carbonated raw material for cement production – use of calcium carbide residue (CCR)	• The type and quality of the clinker produced by CCR are unchanged compared to clinker produced by traditional methods. • Using CCR will avoid significant CO_2 emissions. In a cement plant in Sichuan Province, China, CCR was used to produce 600,000 t of clinker per year. The resulting annual CO_2 emissions reduction was reported to be equal to 224,540 tCO_2 resulting in CO_2 reduction of 374 kg CO_2/t clinker. • When CCR is used instead of limestone, fuel consumption can be reduced because some chemical reactions that would take place if limestone was used will not take place if CCR is used. • The capital cost to implement this technology in two NSP kiln cement plants in China is reported to be between US$2.9 and US$4.3 Million (1 US$= 6.83 Chinese yuan). • Use of CCR in the cement industry mitigates the risk of pollution to environments, especially water resources and surrounding landfills [66–67]	Semi-commercial	[66–68]
Cement with low lime saturation factor	• CO_2 emissions from calcination are reduced in low-LSF cements because of the lower	Semi-commercial	[11], [23], [37], [50]

Table 4 (*continued*)

Technology name	Energy/Environment/Other benefits/ Costs	Commercial status	References
	limestone content in the raw meal compared to the raw meal for cements with higher LSF. • Energy consumption: ○ Thermal energy consumption decreases by 100 MJ/t clinker for an assumed decrease in LSF of 10 (with no production increase assumed). ○ Electric energy increases by 10 to 20 kWh/t cement for an assumed decrease in LSF of 10 [11]. • CO_2 emissions: ○ Indirect CO_2 emissions increase because of increased electricity use. ○ Direct CO_2 emissions decrease because of reduced fuel use and reduced emissions from calcination. • Other raw materials used in place of limestone are usually inexpensive and may be waste products. • For longer hardening periods (~90 day), compressive strength of belite cements is greater than that of ordinary Portland cement. • Early hydration of belite cements is slower than that of ordinary Portland cement. Blending belite cements with ordinary Portland cement to accelerate the initial rate of hydration may produce composite cement suitable for use for many purposes [37], [50].		

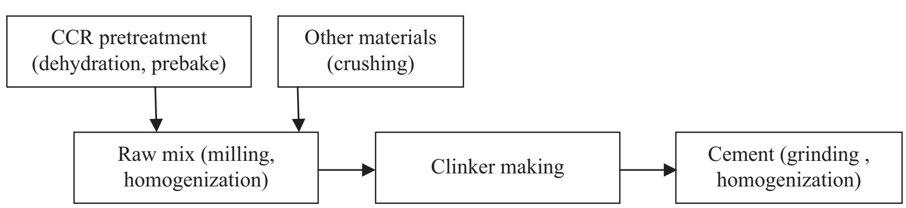


Fig. 3. Flow chart of cement production process using CCR [66].

3) Raw material homogenization
4) Clinker burning
5) De-dusting.

In the first stage, wet CCR is dehydrated, reducing its moisture from 90 percent to the value required according to the moisture content of the other raw materials and kiln type. For the NSP rotary kiln, moisture is reduced to approximately 12–14 percent [66]. For the semi-dry kiln, moisture is reduced to only 65 percent [68]. Because the semi-dry kiln is an older technology that is not promoted anymore, we focus on the use of CCR in NSP rotary kilns. For the NSP rotary kiln, wet CCR is dehydrated by pressure filtration and a spin dryer and transported to the grinding system by a belt conveyor. After grinding, which can be done in a vertical roller mill, the raw material in the CCR is homogenized before being fed to the NSP kiln. A large-scale electric de-duster should be installed on precalcination and cooling systems (Fig. 3) [66].

2.3.4. *Cement with low lime saturation factor*

The lime saturation factor (LSF) in ordinary Portland cement clinker typically ranges between 90 and 102, with average LSFs of up to 97. Higher LSFs are preferred for fast-setting ordinary Portland cements with high compressive strength. Producing Portland cement with very high LSFs (above 100) has several negative consequences. One is increased CO_2 emissions from calcination of greater amounts of $CaCO_3$ in the raw meal, which requires higher burning temperatures. The higher temperatures also mean the clinker granules have denser micro-structure and are therefore more difficult to grind. With regard to resource use, larger volumes of pure limestone are required to achieve higher LSFs. Finally, LSFs higher than 102 will result in large amounts of free lime, which does not contribute to the development of compressive strength and can affect the soundness of the final product [11].

Portland cement with a lower LSF entails fewer CO_2 emissions from calcination because there is less limestone in the raw meal.

Better combustibility of the raw meal means lower burning temperatures, which saves energy. Kiln capacity can also be slightly increased. Additionally, lower LSFs can mean reducing the amounts of valuable pure limestone in the raw meal. A main disadvantage of Portland cement with a low LSF is the reduced alite content and lower compressive strength compared to Portland cement of equal fineness but with a higher LSF. Though compressive strength can be increased to a limited degree by grinding the cement more finely, it is difficult to estimate the electric energy required for the additional grinding. Although less dense clinker with low LSF burned at relatively low temperatures might be easily grindable, additional energy is required to achieve a higher fineness, which is necessary to achieve compressive strength equal to that of Portland cement with a higher LSF; the finer the required texture, the more energy required for grinding [11].

Because a reduction in LSF automatically results in increased belite content, cement with lower LSFs is sometimes called "belite cement." Belite cements are produced at the industrial scale and have reasonably good properties (early strength, compressive strength, etc.). Belite cement can be composed of limestone, burnt clay, volcanic ash, pyrite ash, and gypsum. Reactive forms of belite can be stabilized by rapid cooling, hydraulic activity, and strategies to improve physical–mechanical properties, resulting in a low-energy cement. Mechanical activation of belite has shown promising results to improve the hydration properties of the cement, but the long required grinding time is a disadvantage [23,37].

Campillo et al. [23] analyzed the potential of nanomaterials to improve the initial compressive strength of belite cements. Different nanoparticles were added to belite cement, and the resulting microstructure modifications and mechanical properties were studied. Results indicated that the addition of nanoparticles could improve the initial compressive strength of belite cement so that it was competitive with Portland cement. Other approaches to improve the mechanical strength of belite cements include use of hydrothermal techniques to produce material with a very high specific area [37].

2.4. Emerging alternative cement products

Table 5 shows the energy, environmental and other benefits as well as commercialization status of the emerging alternative cement products. The description of each technology is presented below.

2.4.1. Cement and construction materials based on magnesium oxide

Before Portland cement came into widespread use in the 20th century, magnesium oxide (MgO)- and magnesium chloride-based cements were popular. Today, magnesium-based cements are reported to have compressive strengths ranging from 9000 to 45,000 pounds per square inch (psi) and tension strengths of more than 800 psi, which is many times stronger than conventional concrete. Combined with clays and cellulose, magnesium oxide forms cement that can breathe water vapors electromagnetically. Clay in magnesium oxide also balances and enhances moisture movement, allowing cement that is made with it to continuously expel moisture, which prevents rotting [62].

Table 5
Emerging alternative cement products.

Technology name	Energy/Environment/Other benefits/Costs	Commercial status	References
Cement and construction materials based on magnesium oxide	• For every ton of ordinary Portland cement replaced by Novacem cement, about 0.75 t of CO_2 could be captured and stored indefinitely (Novacem, 2012). Carbon can also be captured during manufacture of Eco-Cement [64] • Ceramicrete expands slightly when it sets and thus forms an excellent seal, in contrast to conventional cements, which contract. • Specialty applications for Ceramicrete can take advantage of its low porosity, nonflammability, strength, and other physical properties. • Ceramicrete makes beneficial use of common waste materials. • No formation energy is required to manufacture Ceramicrete [16]. • Eco-Cement is less alkaline than other hydraulic cements like Portland cement, so Eco-Cement can include more waste [64].	Pilot stage	[16], [45], [62], [64]
Geopolymer cement	• Potential energy and CO_2 savings from the use of geopolymers are significant. • Expected CO_2 emissions for geopolymers are about 300 kg CO_2/t product. This estimate does not take into account emissions from production of the activators, such as sodium silicate, for which no data are available [11]. • Major geopolymer systems rely on minimally processed natural materials or industrial byproducts as binding agents. • The use of industrial byproducts/wastes in the production of geopolymers creates a constructive use for these materials.	Demonstration stage[a]	[11], [19], [33]
Cement primarily of fly ash and recycled materials	• Recycling fly ash to produce concrete avoids the need for landfill disposal of this industrial byproduct. • Use of fly ash reduces or eliminates the need to mine virgin raw materials for Portland cement production and provides a constructive use for waste fly ash. • Increasing use of fly ash will significantly reduce the energy use needed for cement and concrete production. • Increasing use of fly ash can significantly reduce the greenhouse gas footprint of concrete production by eliminating CO_2 emissions from energy use and calcination in cement production. • Using recycled materials as aggregate in concrete diverts these materials from landfills and reduces the need for mined aggregate. Pulverized post-consumer glass is a recycled material that can be used as concrete aggregate.	Semi-commercial	[13], [25], [27], [53]

[a] A short list of companies that are manufacturing and selling geopolymers can be found at: http://www.geopolymer.org/about/business-fellows. This list is not exhaustive.

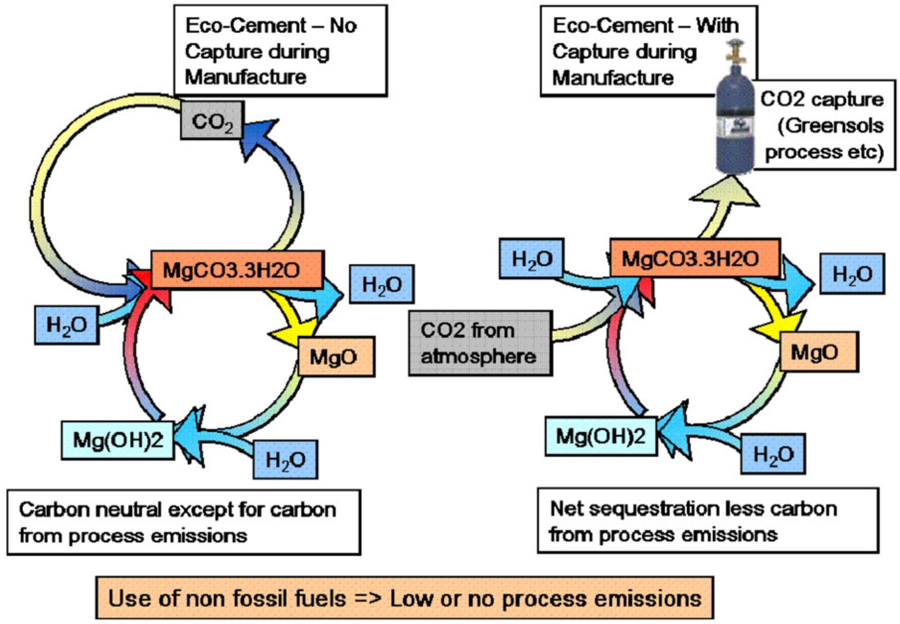


Fig. 4. Eco-Cement CO_2 release and capture during manufacturing [64].

Several entities are producing or have produced MgO-based cements and construction materials that have several environmental benefits. One is Novacem Company, which is developing a new cement production system based on MgO and special mineral additives that lock atmospheric CO_2 into its construction materials. The Novacem process uses magnesium silicates instead of limestone, which eliminates the CO_2 emissions that are normally associated with raw materials processing (calcination). Because the Novacem production system operates at a low temperature, it can take advantage of fuels that have low energy content or carbon intensity (e.g., biomass or municipal solid waste), which further reduces carbon emissions. Carbonates are added to modify the hydration of MgO, which allows the cement to develop compressive strength even when no CO_2 is present. The properties of this alternative cement product are currently being optimized; so far, its performance is acceptable for several applications (e.g., masonry products). Special carbonates that are required for manufacturing the product have a negative carbon footprint because they are produced by carbonating part of the manufactured MgO, and they use atmospheric/industrial CO_2 for this purpose. Novacem claims that the production process to make 1 t of Novacem cement absorbs up to 100 kg (kg) more CO_2 than it emits, making it a carbon-negative product. In addition, because all hydration reactions are reversible, Novacem products can be recycled and used to make new products. Novacem plans to open a pilot plant in 2012 with industry partners. The first entry of the product to the market is expected in 2014–2015 [45].

Argonne National Laboratory and others have licensed several firms to market magnesium-based cements under the name "Ceramicrete." Ceramicrete has many applications ranging from treatment of hazardous waste to consumer products including construction and structural materials requiring high compressive strength, and sealants and coatings. Similar to the process of making cement, the process of forming Ceramicrete requires mixing MgO powder and soluble phosphate powder with water using commercially available equipment. Wet materials are pumped, gunned, or sprayed. The result is a nonporous material that has compressive strength greater than that of concrete. Ceramicrete expands slightly when it sets and so forms an excellent seal, in contrast to conventional cements, which contract [16].

Eco-Cement, developed by TecEco, incorporates reactive magnesia and wastes, and can be used to create concretes that absorb CO_2 and water from the atmosphere. These concretes can be recycled back into Eco-Cement, which is either carbon neutral or negative (i.e., it sequesters carbon) if carbon is captured during its manufacturing (Fig. 4). To make Eco-Cement, magnesite is heated in a kiln to approximately 600–750 °C. Grinding in the hot area of the kiln improves the efficiency of the product. The heating process produces reactive MgO powder that is then added to a predetermined but variable amount of hydraulic cement such as Portland cement; supplementary cementitious materials like fly ash can also be used. The final blended powder is Eco-Cement. When mixed with water and aggregates such as sand, gravel, and waste materials (e.g., ash, plastic, sawdust, slag), Eco-Cement is ready for pouring into concrete, pressing into blocks, or other uses. Because Eco-Cement is less alkaline than other hydraulic cements like Portland cement, reducing the incidence of delayed reactions that would reduce the strength of the concrete, it can include more waste [64].

2.4.2. Geopolymer cement

Geopolymer materials fit in the category of current innovative technology for the construction industry. In contrast to Portland cement, geopolymers rely on minimally processed natural materials or industrial byproducts as binding agents. Potential energy and CO_2 savings from the use of geopolymers are significant. Geopolymer cements that are used as binders are composed of a reactive solid component and an alkaline activator. Reaction with the alkaline agent causes a three-dimensional, inorganic, alumosilicate polymer network to form, which contributes to the high compressive strength of the hardened product. Materials suitable for a geopolymeric polycondensation[1] are alumosilicates, which can be found in nature (metakaolin, natural pozzolana) or industrial wastes (fly ash, GBFS) [11]. Geopolymers are manufactured at relatively low temperatures, with calcining of aluminosilicates occurring at 750 °C. However, no energy consumption data are

[1] Any condensation reaction, of a monomer having two functional groups, which leads to the formation of a polymer.

available for this process [17]. Until now, geopolymers have been produced only for demonstration purposes and used only for non-structural applications such as paving [11]. Other probable applications of geopolymers are bridges and structural retrofits using geopolymer-fiber composites. Geopolymer technology is most advanced in precast applications, which can relatively easily handle sensitive materials such as high-alkali activating solutions and because of the controlled high-temperature curing environment that many geopolymer systems require [69].

Few techniques have been proposed for mass production of geopolymers. The first and only industrial production plant was built in Australia. It is important to note that properties of geopolymer cements depend heavily on the raw materials from which they are made, the chemical composition of the final product, and other features that can affect the properties of concrete such as compressive strength development and crack formation. Another limitation is that reactive components of geopolymers, i.e., fly ash and slag, are industrial waste products whose availability might be limited in some regions. In addition, the highly alkaline conditions under which geopolymers are produced raise an operational safety concern. Production quantities and costs for the alkaline activator (e.g., sodium silicate) are important considerations as well [11].

Pyrament®, a North-American geopolymer application with blended Portland-geopolymer cements, is used successfully for rapid pavement repair [69]. Blue World Crete Company produces a geopolymer that combines a proprietary binding agent with materials containing alumina silicate [19].

2.4.3. Cement/concrete based on fly ash and recycled materials

Using alternative binders in place of Portland cement in concrete reduces the energy consumption and greenhouse gas impacts associated with concrete production. Using an alternative concrete made with fly ash as the binder and pulverized glass as the aggregate further reduces the environmental impacts of concrete production. Fly ash is a byproduct of coal burning that can have cementitious characteristics similar to those of Portland cement. The binding properties of fly ash depend on the type of coal burned and nature of the combustion process that produces the ash. Fly ash usually replaces no more than 25 percent of the Portland cement in concrete. Better understanding of the binding capacities of different types of fly ash might reveal additional possibilities. If the use of fly ash in concrete could be increased, the greenhouse gas footprint of concrete could be reduced. Increasing the amount of fly ash used in concrete would put to practical use large amounts of unused fly ash (39 million tons of fly ash is unused each year in the U.S. according to data from 2004). Ongoing research is focused on developing high-volume-fly-ash concretes. However, these products still use a significant amount of Portland cement [13].

Concrete has also been made using fly ash as the binder and pulverized glass as the aggregate. Aggregate typically accounts for 70–85 percent, by weight, of the material used in concrete. Mining of natural aggregates for the large volumes of concrete produced globally significantly disrupts virgin land. In place of natural aggregates, pulverized post-consumer glass can be used in concrete. Post-consumer glass is readily available in the U.S. which generated 13.2 million tons of glass in 2006, of which only 22 percent was reused [13].

In 2008, Montana State University/Western Transportation Institute performed research using 100-percent fly ash concrete with glass aggregate. This fly-ash-and-glass concrete was used successfully to construct both structural and nonstructural elements of a building. However, further research is required on this new material's fundamental engineering properties [27]. The study identified 96 plants throughout the U.S. as potential sources of ash that could be used as the sole binder for concrete [13]. Using fly ash as the binder and recycled materials as aggregate has a double benefit: it reduces the need to dispose of waste fly ash in landfills as well as the demand for mined aggregate and thus the impacts of mining.

Several existing companies produce cement or precast concrete and other building materials from recycled industrial wastes. One company is RecoCement, which has developed a technology to produce cement made entirely from recycled materials, primarily fly ash. RecoCement products have been tested and produced in small batches by an independent laboratory; the products show satisfactory compressive strength. The company is considering leasing land near the Port of Milwaukee WI, USA, to build a $7-million manufacturing plant for this material [53].

CERATECH is another company that produces cement from fly ash. The company states that its product is successfully used by the U.S. Department of Defense, industrial facilities, state departments of transportation, port authorities, airports, and others [25]. CalStar Products, Inc., also has an innovative technology that uses recycled fly ash as a primary component in architectural facing bricks and durable pavers [22].

2.5. Emerging carbon capture technologies for the cement industry

During cement production, CO_2 is emitted mainly from fuel combustion and limestone calcination. Three basic technologies to capture CO_2 are pre-combustion capture, oxy-fuel combustion, and post-combustion capture (see Fig. 5) [32].

Carbon capture and storage (CCS) is an emerging technology for the cement industry designed to capture and compress CO_2 emissions into liquid form that can be permanently stored deep underground. Because the majority of CO_2 emissions from cement production originate from limestone calcination, pre-combustion technologies do not significantly decrease CO_2 emissions of cement plants; therefore, this CO_2 capture technology is not suitable for the cement industry. It is more appropriate to consider CO_2 capture technologies in the context of cement production process. Oxy-fuel technology uses oxygen instead of air in cement kilns, which results in a pure CO_2 exhaust stream. Oxy-fuel technology is currently being demonstrated in small-scale plants. Further research is required to make this technology a viable option for the cement industry. Post-combustion technologies are end-of-pipe mechanisms that do not need to be fundamentally altered for the clinker-burning process, so these technologies are appropriate for new kilns as well as retrofits [1].

Carbon capture technologies for the cement industry might not be commercially available until 2020. Some pilot projects have begun, for example in California and the UK. Rough estimates of 20–35 Mt/year overall maximum CO_2 emission reduction are made based on 80 percent efficiency and 10–20 large kilns (average 6000 tpd) that are assumed be implemented between 2015 and 2020 globally [1].

Barker et al. [18] assess costs for building new cement plants with post-combustion and oxy-fuel technologies in the UK. The study assumed construction of a dry-process cement plant with a five-stage preheater and precalciner and a cement output of 1 Mt/y. For the oxy-combustion technology, the costs were estimated to be €40/t of CO_2 avoided ($56/t CO_2 using the exchange rate of 1.4$/€) for a 1 Mt/year (yr) cement plant in Europe and €23/t ($32.2/t) for a 3 Mt/yr plant in Asia. These costs are about the same as the cost of the oxy-combustion technology installed at a typical coal-fired power plant. In contrast, the estimated costs of post-combustion capture are substantially higher, equal to €107/t CO_2 ($149.8/t CO_2) for a 1 Mt/yr European cement plant

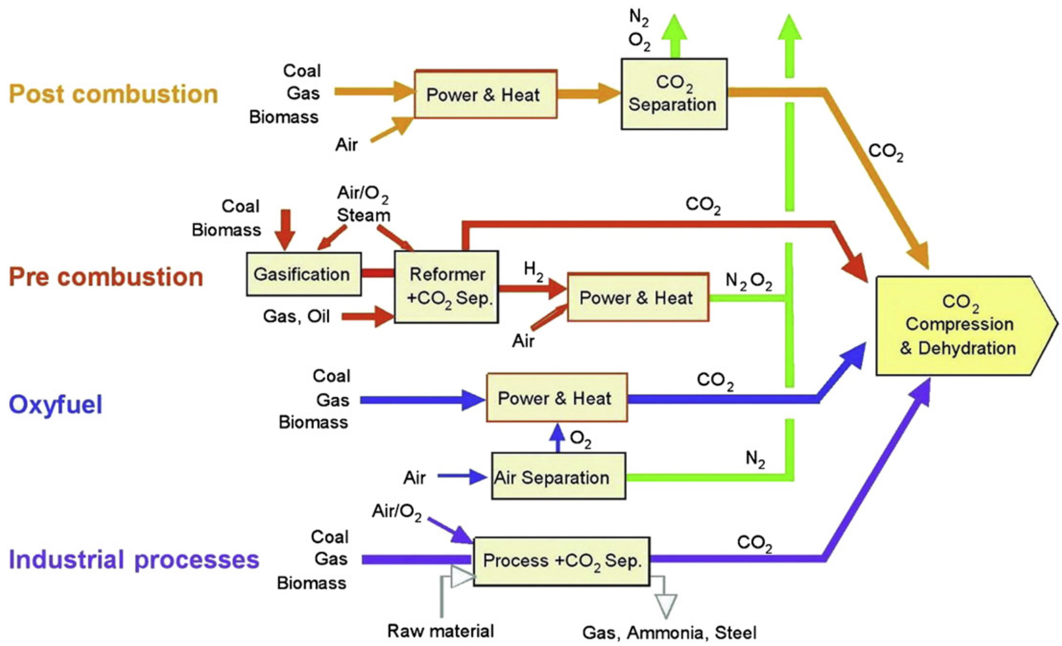


Fig. 5. CO_2 capture technologies [32].
Note: Capture from industrial process streams means application of the abovementioned techniques in the steel industry, cement industry, manufacture of ammonia, alcohols, etc.

and €59/t ($82.6/t) for a 3 Mt/yr Asian plant. These costs are substantially higher than the cost of the post-combustion capture at a power plant, mainly because of lower economies of scale and the need to install flue-gas desulphurization, NO_x reduction, and a steam generating plant for post-combustion capture technology .

Barker et al. [18] state that using oxy-combustion only in the precalciner will avoid approximately 61 percent of the CO_2 emissions that result from traditional cement production. Implementing oxy-combustion in both the precalciner and the kiln could come close to achieving 100 percent avoidance of onsite CO_2 emissions, but significant technical uncertainties remain about this approach. Oxy-combustion requires a sharp increase in onsite power consumption compared to the traditional process. This increase results mainly from oxygen production and CO_2 compression and purification. If we factor in the CO_2 emissions from power generation, the overall reduction in CO_2 emissions attributable to oxy-combustion installed only in the precalciner decreases to from 61 to 52 percent. Table 6 shows the energy, environmental and other benefits as well as commercialization status of carbon capture technologies for the cement industry. The description of each technology is presented below.

2.5.1. Capturing CO_2 emissions from precalcination of limestone

A typical new suspension preheater (NSP) kiln cement plant operates by feeding limestone ($CaCO_3$) to a precalciner that produces CaO by dissociating CO_2 from $CaCO_3$ at high temperatures. Thus, in addition to other products of combustion and excess combustion air, the flue gas from the precalciner contains CO_2 as a result of the calcination of $CaCO_3$ and combustion of the fuel. As a result, the total CO_2 produced in the precalciner is diluted within a larger exhaust stream, making capture of the CO_2 difficult [70]. Rodriguez et al. [55] investigated a novel process using superheated CaO to separate the calcination and combustion reactions into independent chambers. The heat necessary to run the calciner is provided by a stream of high-temperature CaO particles that circulates between a fluidized bed combustor and a fluidized bed calciner. As a result of this arrangement, the exhaust stream from the calciner consists primarily of CO_2. The CO_2 can then be collected and compressed in preparation for storage (Fig. 6). Because more than 50 percent of the CO_2 released in the cement manufacturing process is from calcination, this technology could avoid significant CO_2 emissions from cement plants.

Aspen HYSYS simulations by Rodriguez et al. [54] have demonstrated that this process is theoretically feasible. However, no pilot plant has been built based on this system yet. This technology would be more economical in new plants because retrofits would involve removal of existing preheaters and precalciners (if present) and construction of the fluidized beds, cyclones, heat exchangers, and compressors associated with the CO_2 capture process.

2.5.2. CO_2 sequestration in concrete curing

CarbonCure, Inc., of Canada has developed a concrete curing process that captures CO_2 emissions from their plants as well as neighboring plants and permanently storing the CO_2 in precast concrete products. The capture is accomplished by exposing those products to CO_2-rich flue gases during the concrete curing process. This CO_2 sequestration method had been attempted in the past but was deemed undesirable because of energy required to produce high pressures in the curing chambers. CarbonCure claims that their process can operate at atmospheric pressure without the need for curing chambers. Though this process remains unproven, industry experts believe it holds great potential if successful [34]. Currently, design and industrial testing are in progress to reduce installation and operation risks of the process. The first demonstration plant is projected to start operation in 2012 [24].

Carbon dioxide is naturally reabsorbed in concrete products over hundreds of years through natural chemical reactions. In the CarbonCure process, freshly mixed concrete is exposed to a stream of CO_2-rich flue gas, which speeds up the reactions between the gas and the calcium-containing minerals in cement. As an added benefit, no heat or steam is required, which saves energy and prevents additional CO_2 emissions [34]. The process produces only water and heat as byproducts. With 5 billion tons

Table 6
Emerging carbon capture technologies for the cement industry.

Technology name	Energy/Environment/Other benefits/Costs	Commercial status	References
Capturing the CO_2 resulting from limestone precalcination	• This technology could, theoretically, capture more than 45 percent of the CO_2 released in the cement manufacturing process and avoid about 38 percent of the CO_2 emitted in cement manufacturing (including the CO_2 generated by producing the electrical energy needed for the limestone precalcination process itself). • The cost has been estimated to be about 12 $/t of avoided CO_2 [54].	Research stage	[54–55]
CO_2 sequestration in concrete curing technology	CarbonCure, Inc. claims the following benefits from implementation of carbon curing technology: • 38 percent energy savings compared to conventional precast concrete curing • 17 percent reduction in product greenhouse gas emissions compared to conventional precast concrete • 10 percent cement savings compared to conventional precast concrete curing • 20 percent less product waste • Meets the American Society for Testing and Materials (ASTM) and the Canadian Standards Association (CSA) industry quality standards • Profitable within first year • Less than a day to install the equipment, which means easy retrofit with minimal disruption to existing processes • Capital cost: $8000 [24]. • Use of CO_2 accelerates the curing process and enables it to take place at lower temperatures [46].	Development stage	[24], [38], [42], [46]
Carbonate looping technology	• In addition to the benefit of the CO_2 captured by the calcium looping system, use of the spent precalcined CaO as the raw material for cement production would reduce cement plant CO_2 emissions by more than 50 percent. • Reusing spent sorbent reduces the waste stream. • Using spent sorbent instead of limestone for the cement production conserves natural limestone resources.	Development stage	[28], [36], [47]
Bio-technological carbon capture	According to CO_2 Solution, Inc. their carbon capture technology showed the following benefits at prototype scale [26]: • Use of the enzyme increased CO_2 removal by 30 percent for a given quantity of solvent solution compared to conventional solvent scrubbing technology. • Use of the enzyme lowers capital and operating costs by allowing a reduction in the size of the absorber column and reducing total energy requirements. • When stripping CO_2-rich solvent (desorption), the enzyme can reduce energy consumption by increasing the CO_2 transfer rate. This is significant because, in conventional technology, the desorption stage is a major contributor to the cost of the total CO_2 capture process.	Prototype stage	[26]
Oxygen enrichment and Oxy-fuel technology	• Oxygen enrichment technology reduces fuel use by 100 to 200 MJ/t clinker but increases electricity use by 10 to 35 kWh/t clinker compared to fuel and electricity use in conventional processes [11]. • Short-term experiments have reported a 25- to 50-percent increase in kiln capacity with oxygen enrichment at 30 to 35 percent (volume) in combustion air [11]. • With oxy-fuel technology, overall energy requirements drop by 75 to 84MJ/t cement despite an increase of 92 to 96 kWh/t cement that is attributable primarily to operation of the CO_2 separation, purification, and compression facility as well as the oxygen production [70]. • With oxy-fuel technology, reduction in CO_2 emissions from reduced fuel combustion ranges from 454 to 726 kg CO_2/t cement; however, this would be partially offset by CO_2 emissions increasing by between 50 and 68 kg CO_2/t cement because of increased electricity use [70]. • Using oxy-fuel technology only in the precalciner avoids approximately 61 percent of CO_2 emissions from the process. Using the technology in both precalciner and kiln could avoid almost 100 percent of CO_2 emissions although greater technical uncertainties are associated with this approach [18]. • The additional investment costs for oxy-fuel technology in a new facility are estimated to range from $495 to $540 million, and operational costs would increase by $10 to 13/t cement for a facility producing 2.2 million t/yr. Costs related to transport and storage of CO_2 are not included [70].	Oxy-fuel technology: Pilot stage Oxygen enrichment: Commercial	[11], [18], [31–32], [70]
Post-combustion carbon capture using absorption technologies	• When post-combustion absorption technologies are used, thermal energy consumption increases by 1000 to 3500 MJ/t clinker, and electricity consumption increases by 50 to 90 kWh/t clinker. Overall, primary energy consumption will be high, likely more than 3 MJ per kg CO_2 avoided. • Direct CO_2 reduction potential from a carbon-capture system is up to 750 CO_2/t clinker. Indirect CO_2 emissions increase by 25 to 60 kg CO_2/t clinker because of increased electricity consumption. • A rough estimate is that an investment of $130 to $443 million will be needed for this technology, and operations will cost $13 to $96/t cement, excluding the cost of CO_2 transport and storage [31], [70].	Pilot stage	[11], [18], [20], [31], [70]

Table 6 (*continued*)

Technology name	Energy/Environment/Other benefits/Costs	Commercial status	References
Calera process	• Using less cement and more supplementary cementitious material from the Calera process could reduce CO_2 emissions from concrete production. Calera claims that its process requires less additional energy than many other carbon capture and storage processes if off-peak and low-carbon energy sources are utilized for manufacturing the required alkalinity. • Calera technology focuses not only on capturing CO_2 that would otherwise be released into the atmosphere but also on recycling this CO_2 for concrete production. This is an advantage compared to some other CCS technologies (e.g., post-combustion absorption) in which CO_2 would be stored underground, a technique whose safety and efficacy are still in question. • In addition to capturing CO_2, the Calera technology can capture SO_2 and other acid gases, mercury, and other heavy metals (e.g., silver, arsenic, barium, cadmium, chromium, lead, and selenium) and can safely isolate them in calcium carbonate precipitate [15].	Pilot stage	[15], [21]
Industrial recycling of CO_2 from cement process into high-energy algal biomass	• On average, about 1.8 t of CO_2 will be utilized per ton of dry algal biomass produced. • This technology has significant potential for large-scale reuse of CO_2. • Existing crude oil refineries can use algal oil. • Local use of CO_2 emissions avoids the need for transportation and storage. • Algae cultivation systems can avoid competing with terrestrial food crops, a challenge that has restricted development of first-generation biofuels. • Sewage wastewater can be utilized as a source of nutrients for this technology. • The yield of an algae cultivation system is forecast to be 10 times greater per land area than the yields of terrestrial vegetable oil crops. • This technology could offer a carbon negative pathway in which carbonization is used to produce fuel [46].	Demonstration stage	[17], [46], [49]

of concrete consumed per year worldwide, of which 10 percent is estimated to be precast concrete, there is potential to capture 60 Mt per year of CO_2 through concrete curing if this technology is proven and commercialized. However, sequestration of CO_2 through concrete curing would be exclusively confined to precast concrete plants, and the precast concrete that sequesters carbon is not likely to be favored by the market over existing products. Thus, the product's competitiveness compared to conventionally cured concrete will be determined by the cost savings, reduced curing time, and monetary value of the CO_2 abated through the process [46].

Shao et al. [59] examine the feasibility of this technology and the CO_2 absorption capacities of masonry block, paving stone, cement board, and fiberboard. Capacities were based on the cement content of the products studied and ranged from 6.3 to 18.9 percent within different conditions. Researchers at McGill University are also developing a curing process for the precast concrete industry in which CO_2 is used as a reactant to increase the rates of compressive strength gain in the concrete, to reduce energy consumption levels, and to improve the durability of precast concrete products [38,42].

2.5.3. Carbonate looping technology

Amine scrubbing carbon capture technology uses a significant amount of additional energy that can be reduced by using lime (CaO) as a regenerable sorbent. After reacting with CO_2 for a number of cycles, CaO loses its ability to react with CO_2 and usually becomes waste. However, the exhausted (spent) sorbent could partially replace the main raw material in cement manufacturing, $CaCO_3$. Because the spent sorbent would not need to be calcined in the kiln (releasing CO_2 to form CaO), using it as a replacement for limestone in cement would reduce CO_2 emissions from calcination, which accounts for more than 50 percent of total CO_2 emissions from the cement production process (Fig. 7). This process is also known as a "looping cycle" or "carbonate looping" technology [28].

Abanades describes the fundamentals of the carbonate looping process [14], and Pathi et al. [47] created a model of a simple carbonate looping process based on the average conversion of calcined limestone. The model is used to study the influence of average conversions of limestone in the carbonator on the flow rates of various streams within the looping process, and to study the energy necessary for calciner reactivation. In addition, the model is used to study the carbonate looping process as implemented in the cement pyroprocess [47]. The European Cement Research Academy (ECRA) has estimated that modern anthracite- and lignite-fired power plants emit 750 and 950 g CO_2/kWh, respectively. An 800-MWe power generation plant discharges approximately 620 or 780 tpd of degraded CaO sorbent (the sorbet has a lifetime of 30 cycles). For a mid-sized plant producing 3000 tpd of clinker, use of precalcined CaO could meet approximately one-third of the raw material needs. This looping technology would be feasible if the cement plant and the power plant both function in close cooperation, ideally, next to each other in an operational link [36].

2.5.4. Bio-technological carbon capture

CO_2 Solution, Inc., has taken a biomimetic approach to efficiently capture CO_2 using the natural power of a biocatalyst (enzyme) and carbonic anhydrase, which are substances that manage CO_2 during respiration in mammals. In this technology, the biocatalyst and carbonic anhydrase are used within a reactor to create an "industrial lung" that captures CO_2 from industrial flue gases. After the waste CO_2 is captured, pure CO_2 is produced with the help of the enzyme and then stored underground and/or used in enhanced oil recovery. This technology can be applied to coal-fired power generation, oil sands, and other CO_2-intensive industries such as cement and steel. Prototypes tested at Alcoa Inc.'s aluminum smelting facility in Quebec, Canada, demonstrated the full functionality and stability of the enzyme under real-world conditions [26].

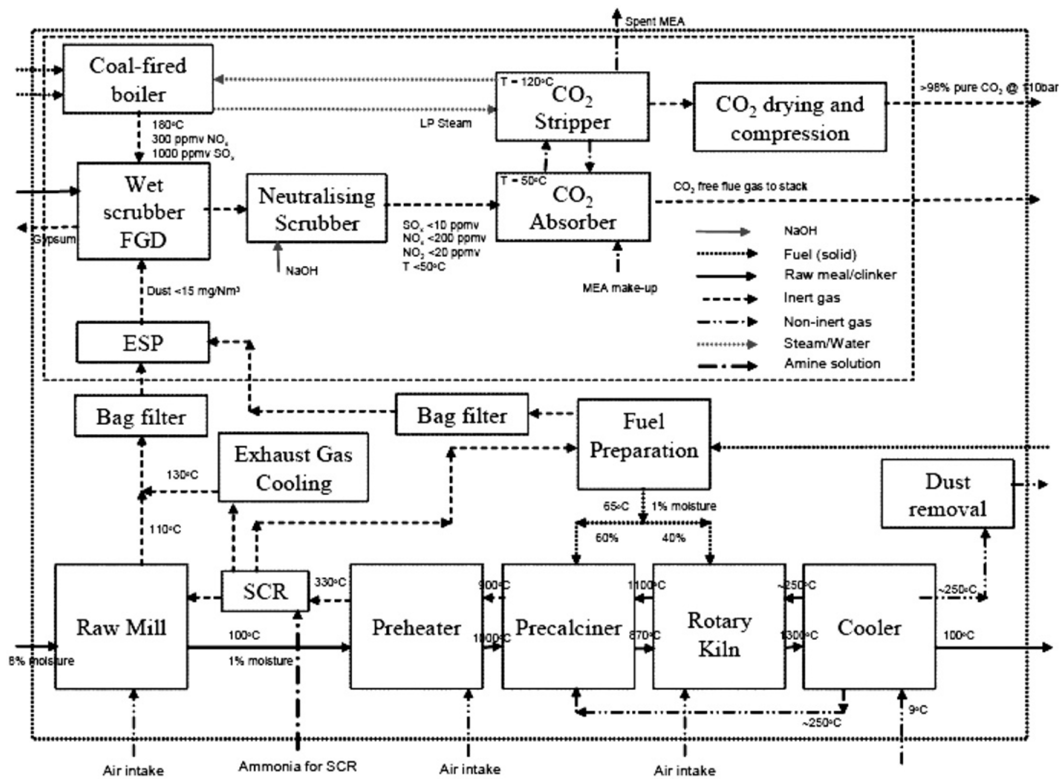


Fig. 6. A cement plant with post-combustion CO_2 capture system [18].

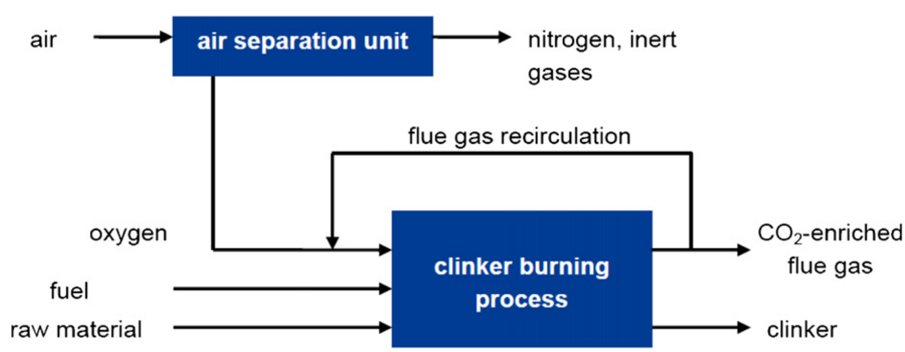


Fig. 7. Oxy-fuel technology with flue gas recirculation [31].

This patented process has three phases. First, flue gas containing CO_2 enters the reactor where it is dissolved or captured in an aqueous solution. CO_2 is then converted into a bicarbonate ion ($HCO_3{}_-$) in the presence of the enzyme. This bicarbonate-ion-enriched solution from the reactor is regenerated either by production of pure CO_2 for underground storage, enhanced oil recovery or other industrial uses; or by production of solid carbonate for various industrial uses. The capture solution is reused in another cycle [26]. Traditional post-combustion CO_2 capture methods are based mainly on amine solvents, which are energy intensive and require high temperatures to strip CO_2 for underground capture and storage. CO_2 Solution, Inc., claims that the enzyme can materially lower the cost of carbon capture by allowing a reduction in the size of the absorber equipment and reducing process energy requirements [26].

2.5.5. Oxygen enrichment and oxy-fuel technologies

The U.S. cement industry has used oxygen-enriched combustion since the 1960s. Using oxygen-enriched combustion air increases energy efficiency, production capacity, and allows fuels with low calorific value to be used in place of fossil fuels. This increases kiln flame temperatures while reducing CO_2 emissions. Short-term experiments have demonstrated a kiln capacity increase of 25–50 percent when combustion air is enriched with 30–35 percent oxygen (by volume). Oxygen enrichment has not yet been applied for purposes of reducing CO_2 emissions. Enriched combustion air might reduce kiln fuel use and thus CO_2 emissions, but additional power is required to produce oxygen, so it is not clear whether there would be a net reduction in total energy use.

Oxy-fuel technology is another emerging candidate for CO_2 capture in new cement kilns. This technology is currently still being researched [31–32]. Oxy-fuel technology differs from oxygen enrichment in that oxygen enrichment does not replace air but injects oxygen into the combustion zone along with combustion air. In contrast, oxy-fuel technology replaces the air with an oxygen stream, using pure oxygen instead of air for fuel burning. Because this eliminates the nitrogen that would normally be in the air that is traditionally used for fuel burning, fuel

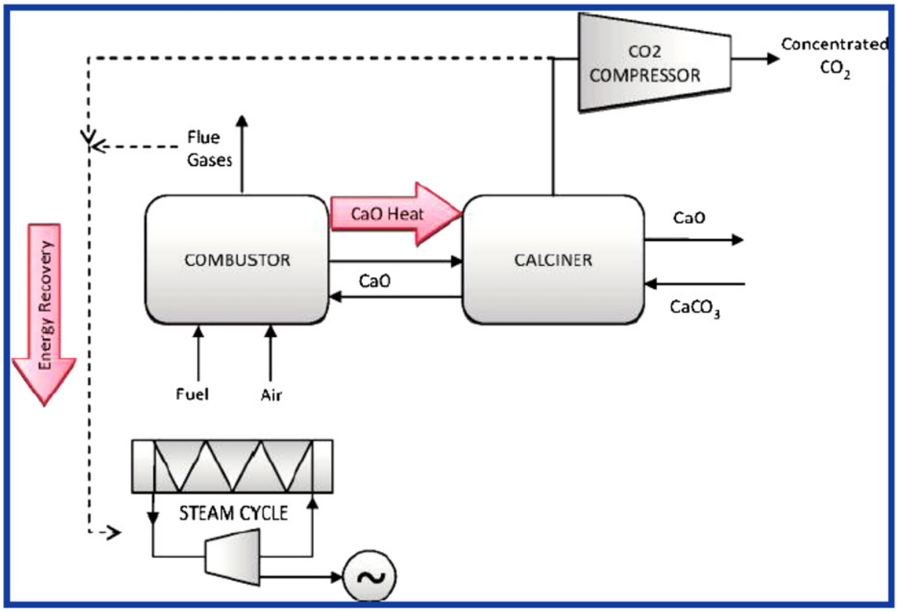


Fig. 8. Schematic of the proposed precalciner for obtaining a CO_2-concentrated stream from the calcination of $CaCO_3$ [54].

requirements and flue gas volumes are reduced. When the oxygen stream is fed to the kiln, the resulting kiln exhaust gas contains up to 80 percent of the CO_2 concentration from the fuel burning. This fraction of the exhaust stream is transported to a CO_2 separation, purification, and compression facility (Fig. 8) [70].

Technical issues associated with the use of oxy-combustion (oxy-fuel technology) at a cement plant include the high flame temperatures (3500 °C) produced by this process which are too hot for proper operation of a cement kiln and the need for recycling a portion of the flue gases back to the combustion zone to provide the necessary dilution; heat-transfer characteristics that are influenced by changing the atmosphere within the combustion chamber; deterioration of kiln walls at higher oxygen levels; clinkering process chemistry under different atmospheres needs further investigation; costly removal of contamination from the CO_2-rich exhaust gas resulting from excessive air infiltration; power consumption increases of 200–240 kWh/t O_2 for oxygen delivery using an air separation unit [18].

2.5.6. Post-combustion carbon capture using absorption technologies

Solvent scrubbing has been used to separate CO_2 in chemical industry exhaust streams [20]. Post-combustion carbon capture takes advantage of this commercially mature technology and applies a common solvent, monoethanolamine (MEA), for CO_2 scrubbing. Because of the high cost of this solvent, it has to be regenerated and reused, an energy-consuming process that results in additional CO_2 emissions. SO_2, NO_2, and oxygen play an important role in solvent degradation mechanisms. Therefore, the SO_2, NO_x, and particulate matter concentrations in flue gases need to be reduced to a minimum before the flue gases go through the solvent scrubbing CO_2 capture system [11].

Barker et al. [18] evaluated several technical issues associated with post-combustion amine scrubbing using MEA in a new cement plant (Fig. 9). These issues include: the concentration of SO_2 in the flue gas for post-combustion capture with amines since amines react with acidic compounds to form salts that will not dissociate in the amine stripping system, problems of solvent degradation associated with NO_x in the flue gas, the need to limit

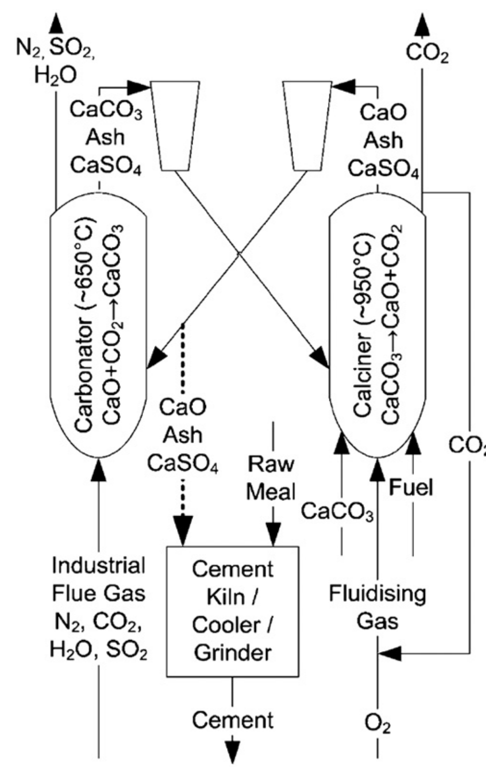


Fig. 9. Flow diagram of calcium-looping CO_2 capture and cement manufacture [28].

dust levels to maintain efficiency of the CO_2 capture process, the need for large amounts of steam for solvent regeneration, maintenance of excess oxygen in the process since the clinker must not be generated in reducing conditions, maintenance of the mandatory temperature range for CO_2 absorption levels (flue gas must be cooled from about 110 °C to about 50 °C), and the influence of acidic components that may reduce the efficiency of the MEA absorption process. Other concerns surrounding amine use

include high costs, energy use for sorbent regeneration, and the potential for degraded solvents to become hazardous wastes. On the other hand, Bosoaga et al. highlights the advantage of higher concentration of CO_2 in the flue gas of cement plants over power plants, thus demanding less power for CO_2 compression [20].

An extensive study by the International Energy Agency (IEA) proposes that cement plants make major changes to implement absorbent technologies. These changes include addition of a solvent scrubber and regenerator as well as a compressor to increase the pressure of CO_2 emissions for transport by pipeline, high-efficiency flue gas desulphurization and de-NO_x to meet flue gas purity requirements, and a combined heat and power plant to provide steam for regeneration of the solvent. The IEA performed a techno-economic analysis of these changes for a new dry-feed-process cement plant located in the UK, with a five-stage preheater and production capacity of 1.1 million tons of cement/yr. The analysis showed that total fuel (coal) consumption for power generation increased by 207.2 MW, and net power consumption from the grid decreased by 13.1 MW (because of onsite electricity generation), compared to fuel and power consumption of a similar cement process without the CO_2 capture system. This takes into account excess electricity generation of 2.9 MW by the combined heat and power plant. Avoided CO_2 emissions were 594,000 t/yr, or 653,200 t/yr, taking into account the import and export of electricity, which showed 74 percent and 77 percent reductions, respectively. The CO_2 savings would have been lower if fuels were not coal. Capital costs increased by \$443 M, and operating costs, taking into account the export of excess electricity generation for the steam plant, increased by \$95.7 M/yr [70].

Absorption technologies are currently only being used at a pilot scale in the energy sector. Demonstration plants are in the planning phase [31], with the first industrial application expected around 2020. With modifications, these technologies should then be available for the cement industry [31]. Availability of a transport (pipeline) grid and storage sites are also important factors necessary to support this CO_2-capture technology.

2.5.7. Calera process

The Calera process captures power-plant CO_2 and stores it as a carbonaceous material. Using a process known as "mineralization via aqueous precipitation," the Calera process converts gas into stable solids such as metastable calcium, magnesium carbonate, and bicarbonate minerals. The process requires a high pH and thus is most economic when power plants are located near sources of suitable brines, which are extracted from geologic formations, as well as alternative sources of alkalinity and minerals. Calera cement is similar to Portland cement and aggregate but can differ by site based on the inclusion of trace components. After processing, the solid materials produced by the Calera process can be used in various construction applications. Calera has another proprietary high-efficiency electrochemical process called "alkalinity based on low energy" which uses only salt and electricity to produce NaOH and HCl ($NaCl + H_2O \text{-} > NaOH + HCl$) [21].

Co-producing electricity with the Calera carbon capture process could reduce power plant emissions by up to 90 percent, with offsetting CO_2 emissions of 10–30 percent from the Calera process (CO_2 emissions associated with the energy use by Calera process). It is possible that Calera supplementary cementitious material could replace 20 percent of ordinary Portland cement in concrete, significantly decreasing concrete's carbon footprint. Challenges associated with the Calera process include dependence on brines extracted from geologic deposits; the need for alternative natural alkalinity resources and/or minerals near the power plant; increase in energy use by Calera process (energy penalty); production of more calcareous material than needed in the current market; potential impact on water balances and hydrology from extraction and reinjection of brines; and the need for environmentally acceptable management of the brines and bicarbonate solutions that must be pumped from and returned to geologic formations as part of the process [15].

Calera has a demonstration project at Moss Landing, California, that is capable of capturing 30,000 t per year of CO_2, which is equivalent to a 10-MW electric (MWe) natural gas power plant [21]. Other Calera demonstrations are planned in California and Wyoming in the USA as well as in China and Australia during the next few years [15].

Another company, Skyonic Corporation, has developed SkyMine® technology, which is a carbon mineralization process that removes CO_2 from industrial waste streams through cogeneration of carbonate and/or bicarbonate materials. A demonstration facility is under construction at Capitol Aggregates, Ltd., cement plant in San Antonio, Texas. This plant is predicted to capture 75,000 t of CO_2 from flue gasses and mineralize the carbon emissions to produce 143,000 t of baking soda, which could be used in industrial applications including as feedstock for bio-algae fuels [46].

2.5.8. Industrial recycling of cement process CO_2 emissions into high-energy algal biomass

Concentrated CO_2 streams produced by cement or power plants could be used to cultivate algae. Due to algae's sensitivity to impurities, the recycled CO_2 would have to undergo a cleaning process before being used for this purpose. Currently, closed algal cultivation systems for biofuel production have moved from the research phase to pilot and demonstration projects. Because of algae's potential as a feedstock for biodiesel production, food products, and chemicals, several large global companies, including BP, Chevron, Virgin, and Royal Dutch Shell, have invested research funding in this area [17].

Commercial-scale systems range from 10 to 100 ha and are estimated to absorb between 500 and 55,000 t CO_2 per system per year. Algae biomass fuels are predicted to become the largest biofuel class by 2022 when they will account for an estimated 37 percent of all biofuels produced. However, large land areas are required for algae cultivation, so the potential for this technology could be limited in areas with high land prices [46]. Similar to existing agricultural systems, algal cultivation requires large quantities of nutrients, which makes it CO_2 intensive. The technical and reliability barriers to this technology are expected to be overcome within 3–5 years, and commercial deployment is expected in 5–10 years [17]. The Cement Task Force of the Asia Pacific Partnership (APP) initiated a project on high-yielding algae culture, with bench-scale development of a cement emissions bioreactor followed by a pilot project and then a commercial-scale demonstration. The current status of the project is not clear. APP predicted 1.2 billion tons per year of algal biomass fuel produced using this technology. The ACC Ltd. Cement plant in India will implement the pilot plant after testing is completed at the Indian Institute of Technology. The total fund for the project was about \$10 million [17]. Another case study by Pond Biofuels, a Canadian company, captures CO_2 and other emissions from a cement plant to create nutrient-rich algae slime. The algae are grown at a facility next to the cement plant to be harvested, dried, and then used as fuel in the plant [49].

Algenol is a U.S. company planning to develop a \$850-million algae plant in the Sonora Desert. Approximately 6 Mt of CO_2 per year would be reused to produce 3.8 million cubic meters of ethanol. Solazyme is another company taking advantage of the microbial fermentation process, fermenting algae on a large scale without the need for sunlight, to produce algae oil. A third company, MBD Energy, uses algae to recycle captured

Table 7
Emerging use of nanotechnology in cement and concrete production.

Technology name	Energy/Environment/Other benefits/Costs	Commercial status	References
Use of nanotechnology in cement and concrete production	• Research has shown the potential for improving concrete properties by modifying the structure of cement hydrates through the addition of nanoparticles and nanotubes, and controlling the delivery of admixtures [52]. • Nanoparticles, such as silicon dioxide, were found to be a very effective additive to polymers and concrete, producing high-performance and self-compacting concrete with improved workability and strength compared to traditional products [61]. • Incorporating nanoparticles allows the increased use of supplementary cementitious materials, reducing the energy need compared to the production of Ordinary Portland Cement.	Research stage	[43], [52], [58], [60–63], [71]

industrial flue-gas emissions and produce algae oils suitable for manufacture of high-grade plastics, transport fuel, and livestock feed [17].

2.6. *Nanotechnology in cement and concrete production*

Nanoscience and nanotechnology are the study and application of extremely tiny particles that can be used in other fields of science, such as chemistry, biology, physics, materials science, and engineering [43]. Nanostructures can be integrated into larger systems. Concrete is a macro-material strongly influenced by the properties of its components and hydrates at the nanoscale [52], [60]. Nanoscience and nanotechnology are being applied to develop cement, alternate cementitious binders, and concrete with improved performance and reduced environmental footprint. To date, research areas are as follows [58], [63], [71]:

- Development of nanocements and eco-friendly, high performance cements/binders manufactured with lower clinker content
- Improvement in cement and concrete performance through incorporation of nanoparticles and chemical admixtures
- Better understanding of cementitious materials through nanoscale investigations of cement hydration reactions and hydration products to achieve cements and concretes with tailored performance
- Development of activators/catalysts for low-temperature clinkerization
- Use of nanoparticles to reinforce cementitious matrices for improved flexibility and toughness
- Application of photocatalytic titanium dioxide nanoparticles for self-cleaning concrete surfaces
- Development of cement-based nanocomposites for various applications

Table 7 shows the energy, environmental and other benefits as well as commercialization status of this technology.

3. Conclusions

This paper describes 18 emerging energy-efficiency and CO_2 emissions reduction technologies for cement and concrete production. The information presented for each technology was collected from various sources, including manufacturers. All the emerging energy-efficiency and low-carbon technologies presented in this paper are alternatives to conventional production of cement and concrete or production of the conventional raw materials used in manufacturing cement or concrete. It is likely that no single technology will be the best or the only solution but instead that a portfolio of technologies should be developed and deployed to address the increasing energy use and CO_2 emissions of the cement industry.

High activation grinding is a very promising emerging technology that can increase the use of additives in cement and concrete production. The FBK is less promising because of its low capacity and also the penetration of highly efficient NSP rotary kilns in the market. The use of carbide slag is a proven technology for reducing CO_2 emissions from clinker production when such material is available. The use of cement with low LSF also can significantly reduce the carbon footprint of cement use for appropriate end-uses. Geopolymers and other alternative types of cements which are produced from waste material (e.g. fly ash) are becoming common and receiving more attention from industry as well as end users. The CCS technologies for the cement industry are at the early stage and it does not seem that they will be widely available at the commercial scale by 2025 or even later. However, given the importance of this group of technologies, extensive research work is being conducted by both public and private sectors and various approaches are being tested.

As can be seen from the information presented in this report, most of the technologies have an energy penalty associated with their operation. Therefore, further research is needed to improve and optimized these technologies in order to minimize their energy penalty. In addition, for some technologies, there was not much information available except from the technology developer. Conducting independent studies and validation on the fundamentals, development, and operation of these emerging technologies can be helpful to private and public sectors as well as academia.

Shifting away from conventional processes and products will require a number of developments including: education of producers and consumers; new standards; aggressive research and development to address the issues and barriers confronting emerging technologies; government support and funding for development and deployment of emerging technologies; rules to address the intellectual property issues related to dissemination of new technologies; and financial incentives (e.g., through carbon trading mechanisms) to make emerging low-carbon technologies, which might have a higher initial costs, competitive with the conventional processes and products. It should be noted that the purpose of this paper is solely informational.

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